

BEAMTIME REPORT CH-3593

"Elucidating the mechanism for deNO_x activity over single site copper in silica aerogels"

We collected high resolution powder X-ray diffraction and transmission XAS data in situ on single-site copper in silica aerogels during separated reaction stages of the SCR-HC-deNO_x process. The XAS data was collected in the quick-scan mode, and powder diffraction data was collected at the end point of individual treatments. The Cu aerogel has previously been studied for SCR-deNO_x in realistic feed (15 % H₂O) with promising results. The aerogels were compared to the microporous xerogel analogue and Cu ZSM-5, the well-established deNO_x catalyst at which poor hydrothermal stability inhibited its commercialization. We conducted three studies of redox cycling in dry and realistic feed (15 % H₂O) in NO/O₂ (0.2 %/2 %) and C₃H₆ (1.3 %). Water was added using a vapor saturator cooled to desired temperature by a chiller.

Some remaining time was given a preliminary study on the formation of bimetallic Au-Cu clusters in silica aerogels and hierarchical SAPO-34 systems (H-SAPO-34) with XAS and powder diffraction. The samples were reduced in H₂ (5 %) to 450 °C using a ramp rate 5 °C/min. The Cu-Au aerogel was treated in alternating feed of C₃H₆ (1.1 %) and O₂ (2.2 %) for speciation in different reaction stages of selective oxidation of propene to acrolein. Both parent materials were found to be highly active and selective for this reaction prior to this beamtime. However, due to time limitations we were not able to conduct the cycling procedure for the H-SAPO-34 system.

Results

Figure 1 shows the XANES (left) and EXAFS results (right) from redox cycling in SCR-deNO_x components (NO/O₂ + C₃H₆) in dry and wet feed at 350 °C for a Cu aerogel, Cu xerogel and Cu ZSM-5. It is well-known that Cu ZSM-5 deactivates in wet feed, thus inhibiting commercialization as a deNO_x catalyst. However, the deactivation from the copper cation perspective has yet to be understood. We find an irreversible alteration of the redox pair Cu²⁺/Cu⁺ in when cycling in wet feed, associated with cation migration to less active sites in the ZSM-5 structure. The Cu xerogel, the hydrophilic and less porous analogue perform poorly as a SCR-deNO_x catalyst in wet feed as well, seen by reversible re-oxidation to Cu²⁺ in C₃H₆/H₂O. The xerogel recovers upon return to dry feed and the active Cu²⁺/Cu⁺ pair was restored, in contrast to Cu ZSM-5. In the Cu aerogel system, the Cu²⁺/Cu⁺ redox pair and local surroundings remain unaffected in the wet feed, thus establishing this system as a promising candidate for further studies in realistic SCR-deNO_x conditions. The powder diffraction data show no

formation of oxidic clusters during the experiment, and we can exclude their presence from our deactivation results.

Figure 2 shows the XANES collected at the Cu K edge and Au L₃ edge upon heating in hydrogen during their reduction. Au reduces from Au³⁺ → Au⁰ at 270 °C, and exhibit nearly identical XANES features as Au foil upon complete reduction. The reduction of Au initializes an abrupt reduction of Cu²⁺ → Cu⁺, and a further reduction to Cu⁰ led to striking alteration of the Au XANES features, establishing a synergetic effect between Au and Cu. Both samples (Cu-Au aerogel and H-SAPO-34) show the formation of bimetallic clusters in this temperature range. We believe the clusters are within the confines of the micropores present in the aerogel and H-SAPO-34 structure. Alternating between C₃H₆ and O₂ for the Cu-Au aerogel led to changes of the Au XANES features upon dynamic redox behavior of Cu. Further studies are needed for the microporous SAPO-34 analogue, and this redox cycling remains for H-SAPO-34 for a complete set of data.

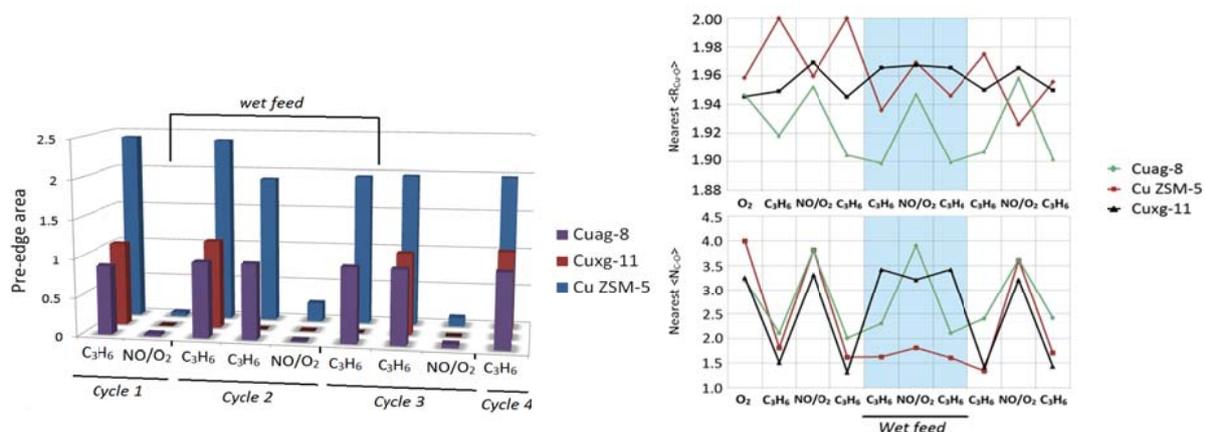


Figure 1: Left: Cu⁺ pre-edge intensity for a Cu aerogel, Cu xerogel and Cu ZSM-5 during redox cycling in dry, wet and dry feed. Right: EXAFS results (Nearest Cu-O shell distances and multiplicity) during the study.

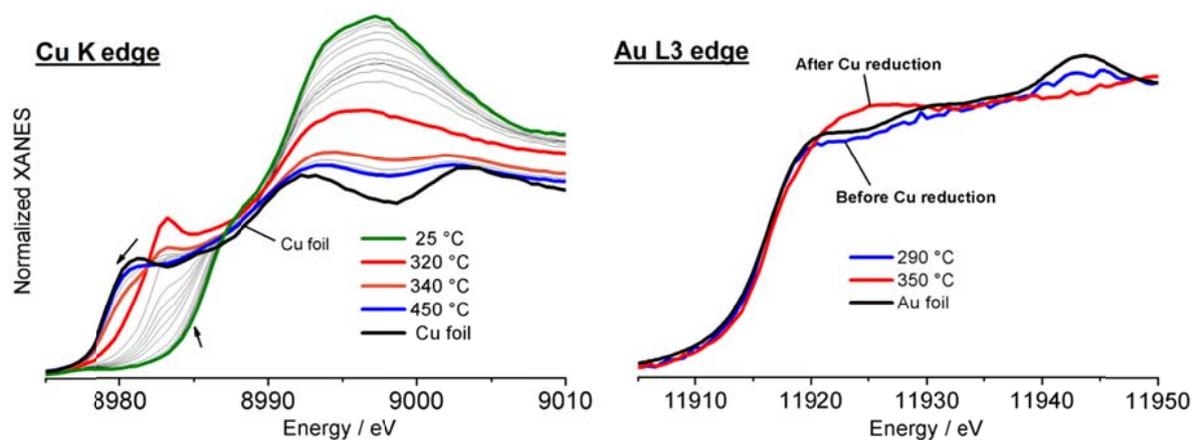


Figure 2: Cu K and Au L₃ XANES collected alternately during hydrogen reduction in a H-SAPO-34 system.